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(54) IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF MIXTURES

(71) We, AGFA-GEVAERT, a naamloze vennootschap organised under the laws of Belgium of 27 Septestraat, B2510 Mortsel, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of a dispersion of a substance in a liquid medium.

The invention provides a method whereby such a dispersion with a very fine disperse phase can be easily formed.

According to the present invention, a dispersion of a substance in a liquid medium is formed by simultaneously and continuously feeding a first liquid which comprises a solution of said substance, and a second liquid which is miscible with said first liquid but is a non-solvent for such substance, through a passageway which is defined by closely spaced surfaces so as to keep that passageway filled with the infed mass of material, while continuously relatively rotating said surfaces so as to subject the mass of material in the passageway to shearing stresses creating turbulence throughout the whole volume of the mass within the passageway.

The fineness of the disperse phase which is attainable by a method according to the invention is due to the subjection of the mass of infed material within the mixing passageway to shearing forces which create turbulence throughout the entire volume of such mass.

An important fact relating to turbulent flow is that while the forces acting on the mass in the flow passageway create within such mass random local currents that are responsible for a large increase in the resistance to movement of the mass, the latter has at every point an average forward velocity component, i.e., a velocity component in the direction in which the mass advances along the passageway. The average forward velocity components at the different points within the flowing mass afford a well defined and predictable velocity profile. Accordingly, the mass in the mixing passageway is subjected to a uniform and predictable mixing action, due to shearing stresses throughout or subsantially throughout its volume. This is in marked contrast to the effect of creating mere turbulence within a body of liquid, e.g. by means of a propeller.

The transition from laminar to turbulent flow is determined by the Reynolds number, this is a critical value giving at the moment of transition the ratio of the energy (erg in the c.g.s. system) necessary for obtaining a velocity v (cm per sec) of the moving liquid mass to the energy used up in friction.

The Reynold's number (Re) is more particularly calculated as follows:

$$\mathrm{Re}=\frac{1 \cdot v \cdot \mu}{\eta}$$

wherein:

1=the diameter in cm of the flow passage cross-section, e.g., the diameter of a tube,

v=flow-through velocity of the liquid mass in cm per sec.,

μ=density of the liquid mass

$$\left(\frac{\text{mass in gram}}{\text{cm3}}\right),$$

η=dynamic viscosity (dyne.sec.cm^{-2}).

The critical Re value at which turbulent flow starts has to be determined experimentally for a given liquid and a given passage.

For example, when water is introduced into the slit-like passage formed by two co-axial cylinders having a smooth surface, if the clearance (c)=r_2-r_1 between the outermost cylinder and inner cylinder is relatively small compared with their respective radii r_2 and r_1, and the outermost cylinder rotates and the inner cylinder is stationary, the critical

[*Price 25p*]

Reynold's number is 1900. If, however, the inner cylinder is rotated and the outer cylinder is stationary, turbulent flow occurs at a much lower tangential velocity. The conditions for the transition from laminar to turbulent flow in a similar system have been defined theoretically and confirmed in practical tests by G. I. Taylor (as referred to on page 175 of "Führer durch die Strömungslehre" by Ludwig Prandtl and others (1969) published by Friedr. Vieweg and Sohn, braunschweig, W. Germany) as follows:

$$Re = U \cdot c/v_k > 41.3\sqrt{r/c}$$

wherein:

U=critical tangential velocity of the inner cylinder,

c=clearance between the cylinders

$$(r_2 - r_1)$$

$$v_k = \frac{\eta}{\mu} = \frac{\text{dynamic viscosity}}{\text{density}}$$

r=mean value of the radii r_1 and r_2 of the inner and outer cylinder respectively.

The method according to the invention can be used for preparing polymer latices and various kinds of colloid dispersions starting from colloid or polymer solutions.

The method according to the invention is of particular practical importance for forming dispersions of organic polymers in aqueous media. When employing the invention for that purpose the first liquid comprises a solution of an organic polymer and the second liquid comprises water or an aqueous medium When preparing dispersions to be used in the manufacture of certain photographic materials it is advantageous to use as the second liquid an aqueous gelatin solution. As a particular example, the invention may be employed for forming a dispersion of polymethylmethacrylate, starting for example with a solution of such polymer in ethyl acetate.

Preferably the mixing passageway is in the form of a layer space which is at all points less than 5 mm in thickness.

A said layer space may, e.g., be defined by two plates, e.g., discs, at least one of which is rotated relative to the other at high speed (e.g. at 10,000—20,000 r.p.m.). The layer space between the plates may, e.g., be of the order of 0.05 mm. The plates may, e.g., be discs having a diameter of 50 cm or less. Larger diameters are not excluded but tend to involve unnecessarily high centrifugal forces.

In the most preferred embodiments of the invention the mixing passageway is in the form of an annular layer space defined by facing surfaces of revolution and the mass within that passageway is maintained in turbulent flow wholly or mainly by frictional forces generated by relative rotation of such surfaces about their common axis of revolution. The surfaces defining the passageway may have a generatrix which is a straight line or a smooth curve or one or each of them may be formed with a helical groove, but in order that liquid in the groove or grooves shall not be shielded from the tangential shearing forces the inclination of the or each groove to the axis of revolution should be in excess of 45°. Apparatus of this kind may, e.g., comprise a body, which is rotatable within a radially symmetrical space defined by a surrounding housing or casing and which defines therewith an annular layer space that can be kept filled by continuously feeding the liquid materials to be mixed into the annular space at one end and continuously discharging the formed dispersion at a corresponding rate from the other end of such space while the inner body is kept in rotation at a sufficient speed to keep the Reynold's number appertaining to the flow of the infed mass along such space above the critical value at which turbulent flow occurs. Of course, the necessary frictional forces for creating turbulence may be generated by rotating the housing relative to the inner body instead of vice versa or by rotating the inner body and the housing in opposite directions. The requisite forces for creating the turbulence may, if desired, be established in part by feeding the liquid materials into the annular passage under pressure, in which case the relative rotational speed of the inner body and housing may be correspondingly reduced. In general, however, it is preferred to feed the liquid materials into the annular space under gravity because the feed system can then be of particularly simple form. The inner and outer bodies can be cylindrical or one or both of them may be of a diameter that varies along the axial length of such body or bodies, preferably in such a manner that the annular space decreases in thickness towards the end thereof from which the formed dispersion discharges. Thus, the inner diameter of the housing may remain constant or decrease, while the external diameter of the inner body increases, or both said diameters may increase but at different rates, or the external diameter of the inner body may remain constant while the internal diameter of the housing decreases. Preferably, however, the internal profile of the housing and the external profile of the inner body taper towards the discharge end so that the annular space decreases towards the discharge end of the space. In all these embodiments the inner body may be located co-axially or eccentrically with respect to the housing, but preferably the housing and inner body are radially symmetrical and co-axial.

The facing walls defining the layer space may be smooth or may have a roughness and/or protuberances, which contribute(s) to create the requisite turbulence. The turbulence can sometimes be promoted by designing or using the apparatus so that the mass within the mixing passage is subjected to frictional forces, due to relative movement of the walls defining the layer space, which vary in magnitude and/or direction from one point to another along the liquid flow path. In the case of a disc type apparatus the tangential shearing forces increase towards the periphery of the layer space. In the case of an apparatus providing an annular space between inner and outer relatively rotating bodies, a change in circumferential velocity and tangential shearing forces will occur if the cross-section of the annular space varies along its length. More or less abrupt changes in angular velocity can also be brought about by varying the speed of relative rotation of the discs or other bodies defining the layer space. In addition or alternatively the direction of rotation of the or each body may be changed during the flow of any quantum of liquid materials along the layer space between the bodies, and/or one or each body may be oscillated in a direction parallel with the inlet-to-outlet flow direction.

Certain apparatus suitable for use in carrying out the invention will be described with reference to the accompanying diagrammatic drawings comprising Figs. 1 to 3 which show three different continuous flow thin film reactors.

The reactor shown in Fig. 1 comprises two discs 1 and 7 which are mounted on hollow shafts 4 and 4′ respectively. The shafts respectively rotate in the directions A and B in bearings in a housing 3 which encloses the discs. The liquids to be mixed are introduced through the hollow shafts so that the liquids come together at the central region of the layer space between the facing surfaces of the rotating discs. These facing surfaces are shaped so that the thickness of the layer space decreases in the radially outward direction.

The discs are rotated at such relative speeds as to generate shearing forces throughout the volume of the liquid mass within the layer space and maintain the mass in turbulent flow. The formed dispersion leaving the periphery of the layer space leaves the apparatus via the bottom outlet 5, 6 of the housing 3.

The mixing apparatus shown in figure 2 comprises a conical body 1 (rotor) rotatably driven by means of a shaft 2 connected to a suitable source of power such as an electric motor. The rotor 1 rotates in a conical chamber 3. The clearance designated (c) between rotor 1 and chamber 3 is variable by means of a regulating means comprising a threaded bolt 4. The liquid materials to be mixed for forming the required dispersion, are introduced through separate feed pipes 5, into the hopper 6 constituted by the upper portion of the apparatus. The formed dispersion is drained off through a pipe 7.

The upper portion of the chamber 3 can be left open as shown, or it may be closed, optionally light-tightly, according to the necessities of the operation to be carried out.

The angles α and β as indicated in figure 2 need not necessarily be the same. The angle γ may vary, e.g., between 0 and 90°. The part of the rotatable body located within the hopper 6 need not necessarily have a conical shape.

The diameters ϕ_1 and ϕ_2 and the heights (h_1) and (h_2) are chosen according to the required mixing time and mixing degree of intensity. Laboratory scale models may have, e.g., rotors with a height of 20 cm and a diameter ϕ_1 of 10 cm. Large scale mixing apparatus for the mixing of rather large amounts of ingredients may have a rotor with a height of about 100 cm and a diameter ϕ_1 of about 50 cm.

The diameter ϕ_2 of the rotor at the drain off opening may be very small provided that the mechanical strength of the lower part of the rotor is sufficient and a proper balancing of the rotor is still possible.

The mixing apparatus according to Fig. 2 is normally operated in a vertical position so that gravity assists the flow of the liquid material to the outlet of the annular mixing passageway. However, the apparatus can be used in an inclined or even a horizontal position. In the latter case the rotor or rotating chamber preferably has a helical profile on its surfaces for conveying the mixture to the outlet.

When the apparatus is considered, e.g., in vertical operation, the liquid materials to be mixed are continuously fed at a controlled rate through the feed pipes and continuously discharge into the annular mixing passageway between rotor 1 and chamber 3. The liquid mass flows downwardly along a helical path within the said annular mixing passageway under the combined action of gravity and the frictional forces on the liquid due to the high speed rotation of the rotor 1. While in the passageway the liquid materials become thoroughly mixed by reason of the shearing forces, which are generated throughout substantially the entire volume of the liquid in the passageway, the whole of such liquid being in turbulent flow. Only very small quantities of liquids come into contact at any moment in the inlet end of the mixing passageway. Such quantities are constrained always to move away from that inlet end towards the discharge end. If the reactants were to be fed at such a rate that they flow over and come into contact above the rotor rather than within the annular passageway, the result would be an increase in the average

particle size of the discontinuous phase of the dispersion. In accordance with a preferred feature, the thickness of the annular passage between the chamber 3 and the rotor is made variable by the provision of the adjustment means 4.

By way of modification, the rotor and housing could be of other than conical form. For example, the rotor could be shaped according to a curve forming part of a parabola, hyperbola or ellipse. In such a case the diameter of the rotor could still decrease from diameter ϕ_1 to diameter ϕ_2.

According to another embodiment, a rotor is used, which is of generally conical form but has a helical peripheral groove of constant or varying pitch. The crests and grooves may, e.g., be of conical, square, sinusoidal, semi-circular or any other required shape.

An example of an apparatus with a helically grooved rotor is shown in Fig. 3. This apparatus comprises a helically grooved rotor 1 having a spindle 2 by which the rotor is rotated in the direction indicated by the arrow. The rotor rotates in a stationary housing 3 between the inner surface 6 of which, and the periphery of the rotor, a layer space is formed. The diameter of the housing decreases downwardly so that the clearance between the surface 6 and the bottom of the helical groove in the rotor decreases from the top to the bottom of the layer space. The liquid materials to be mixed are separately fed into the annular space at the top thereof and the formed dispersion discharges from the bottom of such space, through the axial outlet 7 of the housing.

The following are specific examples of a method according to the invention.

Example 1

A dispersion of ethylcellulose in an ethanol water mixture was prepared by means of apparatus as shown in Fig. 2.

The height (h_1) of the rotor part in the conical chamber was 122 mm. The height (h_2) was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The angles α and β were both 10°. The rotor was made of stainless steel and had a smooth surface.

The starting liquids used were water and a 5% by weight solution in ethanol of Ethyl Cellulose N7 (trade mark of The Hercules Powder Company Inc., Wilmington, Del., U.S.A. for an ethylcellulose that is insoluble in a mixture of equal volumes of water and ethanol). These liquids were separately fed into the annular space between the rotor and housing of the mixing apparatus.

The rotor speed was 930 rpm, the thickness of the annular mixing passageway 0.44 mm, and the temperature of the liquids 20°C.

The water was introduced at a rate of 104 ml per min. and the ethylcellulose solution at 14 ml per min.

A batch process operating with high speed stirrer (mixing turbine impeller) wherein the same liquids in the same volume ratio were used, yielded a much coarser dispersion than than obtained by means of the continuous turbulent flow mixing device according to this example.

Example 2

The following two solutions were prepared separately:

(A) a solution of 150 g of polymethylmethacrylate dissolved in 750 ml of ethyl acetate,

(B) a solution of 300 g of gelatin dissolved in 2100 ml of water containing 24 ml of a 20% by weight aqueous solution of the dispersing agent MERSOLAT (trade name for a sulphonated paraffin of Bayer A.G., Leverkusen, W.-Germany).

Said solutions A and B were introduced simultaneously in the annular passage of a mixing vessel having a housing and rotor as diagrammatically represented in Fig. 2.

The height h_1 of the rotor part in the conical chamber was 122 mm. The height h_2 was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The angles α and β were both 10°. The clearance (C) was 1.7 mm.

The angular speed of the rotor during the mixing was 1030 rpm.

The solutions (A) and (B) were introduced in the following proportions:

Solution (A): 70 ml per min.
Solution (B): 92 ml per min.

Working under these conditions the contact time of the reactants in the clearance (thin film) was about 2.0 sec.

The temperature was kept constant at 44°C during the dispersing.

The mean diameter of the dispersed polymethyl methacrylate particles was 5000 nm. The mean diameter of the particles was determined by microscopic measurement.

The particle size distribution of the globules obtained by this procedure was much more homogeneous than could be obtained in a batch process dispersing technique. Moreover, the present continuous flow thin film mixing process allows the use of much more concentrated polymer solutions and the use of less dispersing agent and gelatin as protective colloid.

WHAT WE CLAIM IS:—

1. A method wherein a dispersion of a substance in a liquid medium is formed by simultaneously and continuously feeding a

first liquid which comprises a solution of said substance, and a second liquid which is miscible with said first liquid but is a non-solvent for such substance, through a passageway which is defined by closely spaced surfaces so as to keep that passageway filled with the infed mass of material, while continuously relatively rotating said surfaces so as to subject the mass of material in the passageway to shearing stresses creating turbulence throughout the whole volume of the mass within the passageway.

2. A method according to claim 1, wherein the said first liquid comprises a solution of an organic polymer and said second liquid comprises water or an aqueous medium, the method resulting in the formation of a dispersion of said polymer.

3. A method according to claim 2, wherein said second liquid comprises an aqueous gelatin solution.

4. A method according to claim 2 or 3 wherein said organic polymer is polymethylmethacrylate.

5. A method according to claim 4, wherein said first liquid comprises a solution of polymethylmethacrylate in ethyl acetate.

6. A method according to any preceding claim, wherein the said passageway is in the form of a layer space which is at all points less than 5 mm in thickness.

7. A method according to any preceding claim, wherein the said passageway is in the form of an annular layer space defined by the outer and inner surfaces respectively of inner and outer bodies, and the bodies are relatively rotated to generate shear forces for maintaining the mass within the passageway in turbulent flow.

8. A method according to claim 7, wherein each of said surfaces has a generatrix which is a straight line or a smooth curve.

9. A method according to claim 7 or 8, wherein the said surfaces taper from one end of said annular space, at which the liquids are fed into it, towards the other end of such space at which the formed dispersion discharges therefrom.

10. A method according to claim 1 and substantially according to either of the Examples herein.

11. A method according to any of claims 1 to 9, wherein the apparatus used is substantially as herein described with reference to Fig. 2 of the accompanying drawings.

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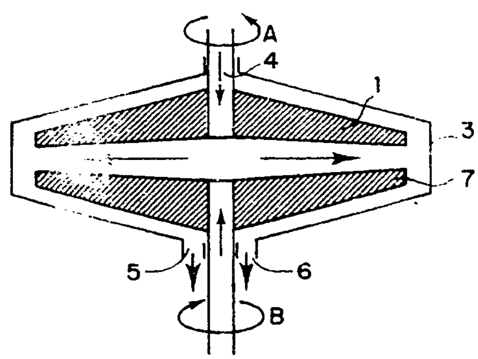

FIG 1

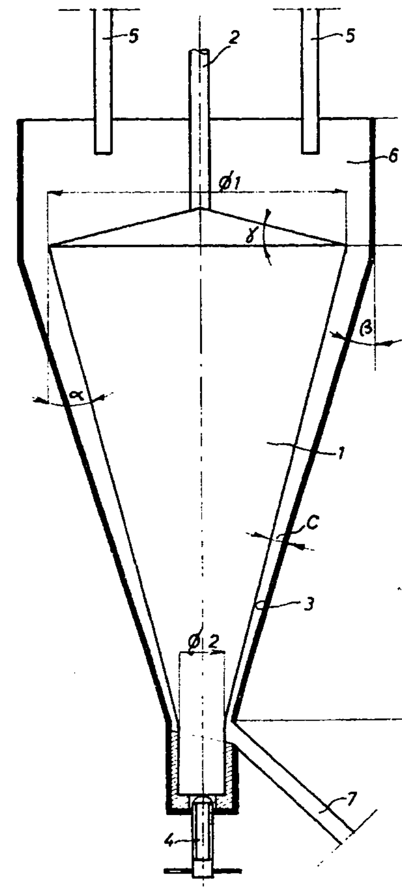

FIG 2

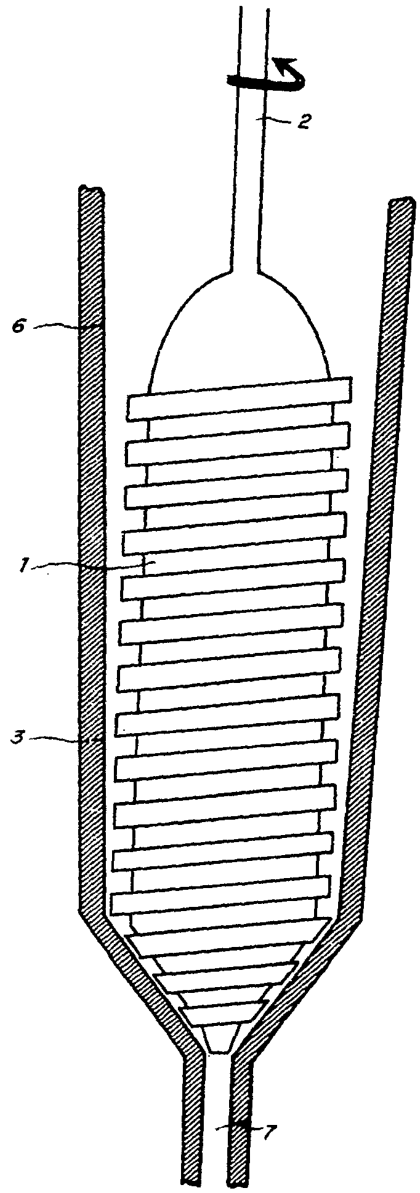

FIG 3